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Glycylglycinatocopper(II) Dihydrate*

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Glycylglycinatocopper(II) dihydrate, $[(O_3N_2C_4H_6)Cu].2H_2O$, crystallizes in the monoclinic system, systematic absences hkl, $h+k=2n+1$ and $h0l$, $l(h)=2n+1$ consistent with the space groups Cc and $C2/c$, with $a=12{\cdot}488$ (5), $b=9{\cdot}245$ (6), $c=13{\cdot}360$ (5) Å, $\beta=97{\cdot}68$ (3)°, $V=1528{\cdot}60$ Å^3, $Z=8$, $D_m=2{\cdot}00$ (1), $D_c=1{\cdot}996$ g cm^{-3}, $\mu(\text{Mo } K\alpha)=29{\cdot}6$ cm^{-1}. Intensities for 2229 independent reflections were collected by counter methods. The structure was solved by standard heavy-atom methods ($C2/c$) and refined by full-matrix least-squares calculations, based on F, to a final R value of 0·038. The final weighted R value and goodness-of-fit are 0·045 and 1·8, respectively. The coordination sphere about the copper atom is square pyramidal with the tridentate glycylglycine dianion and one water molecule, Cu–O distance 1·946 (1) Å, completing an approximate square plane and the second water molecule, Cu–O distance 2·383 (1) Å, occupying an apical position. The crystal contains an extensive array of hydrogen bonds and a weak dimerization of the complexes about centers of symmetry.

Introduction

We have recently initiated a systematic study of several complexes obtained by the reaction of glycylglycinatocopper(II) with substituted and unsubstituted purines and pyrimidines (Kistenmacher, Szalda & Marzilli, 1975). Our interest in these systems stems primarily from an attempt to understand clearly the role played by interligand interactions (*i.e.* interactions between two or more ligands in the coordination sphere of a metal complex) in determining the preferential site for complexation to multi-site ligands (Marzilli, Kistenmacher, Darcy, Szalda & Beer, 1974). In particular, we are interested in multi-site ligands (*e.g.* purines and pyrimidines) where electronic effects play only a small role in binding-site selectivity.

As an aid in the interpretation of these binding site studies, we wished to examine in detail a complex of glycylglycinatocopper(II) where no interligand interactions were present. An obvious choice for such a study is the complex of glycylglycinatocopper(II) with water. Prior to the present work, structural data on glycylglycinatocopper(II) trihydrate appeared (Hermodsson & Strandberg, 1957; Strandberg, Lindqvist & Rosenstein, 1961; Freeman, 1967). However, until very recently structural parameters based on accurate data were unavailable (Freeman, 1974). We have been able, by a slight modification of a synthetic route to the monohydrate (Manyak, Murphy & Martell, 1955), to obtain crystals of glycylglycinatocopper(II) as the dihydrate.

Experimental

The preparation of glycylglycinatocopper(II) followed essentially from the method of Manyak *et al.* (1955). 2·4 g of $Cu(NO_3)_2.3H_2O$ (0·01 mole) was dissolved in water and converted to copper hydroxide by the addition of 50 ml of 1N NaOH. The precipitate was thoroughly washed with water. A suspension of the hydroxide was treated with 1·32 g of glycylglycine (0·01 moles). The deep-blue solution was then filtered and allowed to evaporate slowly. After several days, deep-blue crystals of the dihydrate formed.

Crystals of the dihydrate are monoclinic prisms with [101] as the prism axis. Preliminary photographs indicated a monoclinic lattice with systematic absences hkl, $h+k=2n+1$; $h0l$, $l(h)=2n+1$ consistent with the space groups Cc and $C2/c$. Unit-cell dimensions and their associated standard deviations were obtained

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from a least-squares fit to the 2θ, ω and χ values for 14 carefully centered reflections. The density was measured by neutral buoyancy methods and indicated eight formula units of $[(\text{glygly})\text{Cu}^{\text{II}}].2H_2O$, where glygly is the dianion of glycylglycine, per unit cell.

Intensity measurements were made on a Syntex $P\bar{1}$ computer-controlled diffractometer equipped with a graphite monochromator crystal. The crystal used in data collection had dimensions 0·20 × 0·25 × 0·30 mm with the long axis approximately aligned along the φ axis of the diffractometer. Intensity data were collected with Mo $K\alpha$ radiation by the θ–2θ scan technique. Individual scan speeds were determined by a rapid scan at each Bragg peak, and the rate of scanning ranged from 1·5° min^{-1} (less than 100 counts during the rapid scan) to 24° min^{-1} (more than 1000 counts during the rapid scan). Three standards were measured after every 100 reflections during the course of the experiment, and their intensities showed no unusual fluctuations or decay with time. All reflections in the quadrant hkl–$hk\bar{l}$ were surveyed ($2\theta_{\max}=60°$); these totaled 2522 reflections including standards, glide absences and some symmetry-related data. The 2230 independent reflections were assigned observational variances based on the equation:

$$\sigma^2(I)=S+(B_1+B_2)\,(T_S/2T_B)^2+(pI)^2,$$

where S, B_1 and B_2 are the scan and individual extremum background counts, T_S and T_B are the scan and individual background counting times ($T_B=\frac{1}{4}T_S$) and p was taken to be 0·03 and represents the expected error proportional to the diffracted beam intensity (Busing & Levy, 1957). The intensities and their standard deviations were corrected for Lorentz and polarization effects, but no correction for absorption was applied [$\mu=29{\cdot}6$ cm^{-1}; maximum error in I due to the lack of absorption correction is about 7 %]. The intensities were placed on an approximate absolute scale by the method of Wilson (1942).

Solution and refinement of the structure

The centrosymmetric space group $C2/c$ was indicated by intensity statistics and has been used throughout. The successful solution and refinement (see below) confirm the space-group choice. The position of the copper atom was determined from an unsharpened Patterson map. A subsequent structure-factor Fourier calculation ($R=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}42$) allowed the positioning of the remaining 11 independent heavy atoms. Four cycles of isotropic least-squares refinement, minimizing the quantity $\sum w(|F_o|-|F_c|)^2$ where $w=1/\sigma^2(F_o)$, reduced R to 0·16. A difference Fourier map was then computed, and all ten independent hydrogen atoms located.

The refinement was continued, adding successively to the parameter list: (1) anisotropic thermal parameters for the heavy atoms; (2) coordinates for the hydrogen atoms; (3) isotropic temperature factors for the hydrogen atoms. The 004 reflection was excluded from these final cycles of refinement, $|F_o|=466$e, $|F_c|$ about 586e; the large difference in the observed and calculated structure-factor amplitudes being attributed to extinction effects. The final R value is 0·038. The final weighted R value $\{[\sum w(F_o-F_c)^2/\sum wF_o^2]^{1/2}\}$ and goodness-of-fit $\{[\sum w(F_o-F_c)^2/(NO-NV)]^{1/2}$ where $NO=2229$ independent observations and $NV=149$ parameters$\}$ are 0·045 and 1·8, respectively.

The scattering factors for all heavy atoms were taken from the compilation of Hanson, Herman, Lea &

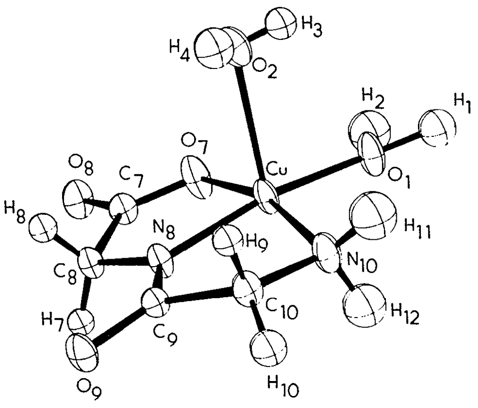

Fig. 1. A perspective view of the complex glycylglycinatocopper(II) dihydrate. The thermal ellipsoids are drawn at the 40 % probability level.

Table 1. *Final heavy-atom parameters* ($\times 10^4$)

Estimated standard deviations are in parentheses. The form of the anisotropic ellipsoid is $\exp\,[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	1983 (0·2)	2179 (0·2)	1265 (0·2)	21 (0·2)	40 (0·3)	51 (0·2)	−2 (0·1)	6 (0·1)	−1 (0·2)
O(1)	3472 (1)	2535 (2)	1052 (2)	29 (1)	55 (2)	78 (1)	−3 (1)	15 (1)	−0 (1)
O(2)	2455 (1)	2011 (2)	3049 (1)	35 (1)	66 (2)	54 (1)	−1 (1)	2 (1)	9 (1)
O(7)	1598 (1)	4250 (2)	1260 (1)	31 (1)	43 (2)	91 (1)	−7 (1)	10 (1)	−2 (1)
O(8)	237 (1)	5782 (2)	1251 (1)	50 (1)	44 (1)	67 (1)	7 (1)	12 (1)	0 (1)
O(9)	−917 (1)	275 (2)	1184 (1)	27 (1)	51 (2)	53 (1)	−10 (1)	9 (1)	−2 (1)
N(8)	463 (1)	1935 (2)	1205 (1)	21 (1)	43 (2)	42 (1)	1 (1)	5 (1)	4 (1)
N(10)	1969 (1)	5 (2)	1050 (1)	29 (1)	48 (2)	55 (1)	5 (1)	7 (1)	0 (1)
C(7)	596 (2)	4530 (2)	1224 (2)	36 (1)	41 (2)	40 (1)	−1 (1)	6 (1)	0 (1)
C(8)	−180 (2)	3242 (2)	1156 (2)	25 (1)	41 (2)	38 (1)	−0 (1)	6 (1)	2 (1)
C(9)	72 (1)	631 (2)	1210 (1)	26 (1)	41 (2)	27 (1)	1 (1)	4 (1)	2 (1)
C(10)	920 (2)	−555 (2)	1279 (2)	29 (1)	35 (2)	40 (1)	1 (1)	5 (1)	−0 (1)

Skillman (1964); the form factor for H was that of Stewart, Davidson & Simpson (1965). The real part of the scattering curve for Cu was corrected for anomalous dispersion effects (Cromer, 1965). Final heavy-atom parameters are collected in Table 1, while those for the hydrogen atoms are given in Table 2.*

Table 2. *Final hydrogen-atom coordinates* (× 10^3) *and isotropic thermal parameters*

The heavy atom to which the hydrogen atom is attached is given in square brackets. Estimated standard deviations are in parentheses. The form of the isotropic thermal parameter is $\exp[-(B\sin^2\theta/\lambda^2)]$.

	x	*y*	*z*	*B*
H(1) [O(1)]	426 (2)	197 (3)	116 (2)	3·4 (6)
H(2) [O(1)]	375 (3)	333 (4)	108 (2)	4·8 (8)
H(3) [O(2)]	301 (2)	166 (3)	315 (2)	2·2 (5)
H(4) [O(2)]	215 (2)	150 (3)	324 (2)	3·3 (7)
H(7) [C(8)]	−66 (2)	334 (2)	52 (1)	1·8 (4)
H(8) [C(8)]	−45 (2)	335 (3)	176 (2)	1·9 (4)
H(9) [C(10)]	95 (2)	−90 (2)	196 (2)	1·7 (4)
H(10) [C(10)]	73 (2)	−122 (3)	82 (2)	2·5 (5)
H(11) [N(10)]	252 (3)	−59 (4)	140 (2)	4·4 (8)
H(12) [N(10)]	205 (3)	−15 (3)	35 (2)	3·9 (6)

The structure-factor and Fourier calculations were performed using the X-RAY 67 series of programs (Stewart, 1967); the least-squares refinements were performed with an extensively modified version of *ORFLS* (Busing, Martin & Levy, 1962); best planes were computed with the program of Pippy & Ahmed (1968); the illustrations were prepared with the aid of the computer program *ORTEP* (Johnson, 1965). All other calculations were performed with locally written programs.

Discussion

The crystal structure contains discrete units of [(glygly)Cu^{II}].2H_2O in which the copper has approximately square-pyramidal coordination (Fig. 1). The equatorial plane is defined by the tridentate glycylglycine dianion and a strongly bound water molecule, Cu–O(1) distance 1·946 (1) Å. The coordination sphere about the copper is completed by a loosely bound axial water molecule, Cu–O(2) distance 2·383 (1) Å. The molecular geometry of the complex found here is similar to that observed in [(glygly)Cu^{II}].3H_2O (Strandberg, Lindqvist & Rosenstein, 1961) and to other copper(II) complexes where a weak axial bond is formed (Hathaway, 1973). The heavy-atom bond lengths and angles (Table 3) are in good agreement with those found in the trihydrate (Freeman, 1974).

Table 3. *Heavy-atom bond lengths* (Å) *and angles* (°)

Bond-length estimated standard deviations: Cu–O(N) 0·002, C–C(N, O) 0·003 Å. Bond-angle estimated standard deviations: N(O)–Cu–N(O) 0·1, Cu–N(O)–C 0·2, N(C, O)–C(N)–N(C, O) 0·3°.

Cu—O(1)	1·946	C(9)–O(9)	1·274
Cu—O(2)	2·383	C(9)–N(8)	1·301
Cu—O(7)	1·974	N(8)–C(8)	1·447
Cu—N(8)	1·903	C(8)–C(7)	1·530
Cu—N(10)	2·030	C(7)–O(7)	1·272
N(10)–C(10)	1·478	C(7)–O(8)	1·244
C(10)–C(9)	1·519		
N(10)–Cu—N(8)	83·5	C(10)–C(9)–O(9)	118·7
N(10)–Cu—O(7)	164·2	C(10)–C(9)–N(8)	114·2
N(10)–Cu—O(1)	97·9	O(9)—C(9)–N(8)	127·0
N(10)–Cu—O(2)	94·2	Cu—N(8)–C(9)	118·9
N(8)—Cu—O(7)	82·7	C(9)—N(8)–C(8)	124·6
N(8)—Cu—O(1)	168·8	Cu—N(8)–C(8)	116·6
N(8)—Cu—O(2)	98·4	N(8)—C(8)–C(7)	107·7
O(7)—Cu—O(1)	94·2	C(8)—C(7)–O(7)	117·1
O(7)—Cu—O(2)	95·4	C(8)—C(7)–O(8)	119·9
O(1)—Cu—O(2)	92·5	O(7)—C(7)–O(8)	123·0
Cu—N(10)–C(10)	108·0	Cu—O(7)–C(7)	115·8
N(10)–C(10)–C(9)	111·4		

A point of some interest is the planarity of the glygly chelate system. It is well known that substitution of a coordination bond for the proton at the peptide nitrogen atom, N(8), causes the chelated glygly ligand to be roughly planar while the free amino acid is distinctly non-planar (Strandberg *et al.*, 1961; Freeman, 1967). The glygly ligand in [(glygly)Cu^{II}].2H_2O is in accord with this general result. There is an approximate folding of the chelated moiety about the Cu–N(8) bond,

Table 4. *Distances* (Å) *and angles* (°) *in the interatomic contacts of the type, D*–H···*A*

D	H	*A*	*D*–H	*D*···*A*	H···*A*	∠*D*–H···*A*
Strong hydrogen bonds						
O(1)	H(1)	O(8)^a	1·11 Å	2·720 Å	1·63	166
O(1)	H(2)	O(9)^b	0·81	2·645	1·85	168
O(2)	H(4)	O(9)^c	0·68	2·800	2·13	167
Weak or bifurcated hydrogen bonds						
O(2)	H(3)	O(8)^d	0·76	3·123	2·38	170
O(2)	H(3)	O(7)^d	0·76	2·911	2·40	126
N(10)	H(11)	O(2)^d	0·95	3·065	2·34	133
N(10)	H(12)	O(9)^e	0·96	3·107	2·33	137

Symmetry code: (*a*) $\frac{1}{2}+x, -\frac{1}{2}+y, z$; (*b*) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (*c*) $-x, y, \frac{1}{2}-z$; (*d*) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (*e*) $-x, -y, -z$.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30910 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

dihedral angle of 5·3 (3)°, such that the two halves of the chelate system are each more planar than the ligand as a whole. The carboxylate and peptide groups have retained their expected planarity, and the steric requirements associated with this retention of planarity in these groups and the formation of the Cu–N(8) bond probably precludes a more coplanar arrangement of the complete ligand framework. The copper atom, as in the trihydrate, is significantly displaced from the equatorial plane about 0·13 Å toward the loosely bound water molecule. In this respect, it is interesting that the copper lies nearly in the plane of the carboxylate half of the ligand (deviation 0·006 Å), while it lies substantially out of the plane of the peptide half of the ligand (deviation 0·091 Å).

The crystal packing in [(glygly)Cu^{II}].2H_2O is dominated by a series of intermolecular hydrogen bonds involving all of the acidic protons in the complex (Table 4). As noted in the structure of glycylglycinatocopper(II) trihydrate (Strandberg, Lindqvist & Rosenstein, 1961), the strongly coordinated water molecule [O(1)H_2] forms two strong hydrogen bonds while the loosely bound water molecule [O(2)H_2] is involved in a weaker set of hydrogen bonds.

There also seems to be some contribution to packing stability owing to the presence of weak dimerization of the complexes about centers of symmetry $(\frac{1}{2}-x,\frac{1}{2}-y,-z)$ involving Cu and O(1) [Cu–O(1) distance 3·083 (1) Å]. This weak dimerization extends, in a very qualitative sense, the coordination of the copper from five to six.

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Refinement of the Crystal Structure of Fe_3BO_6

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Fe_3BO_6 is orthorhombic with $a=10{\cdot}048$ (2), $b=8{\cdot}531$ (2), $c=4{\cdot}466$ (1) Å, space group *Pnma* (No. 62), $Z=4$. It is isostructural with the mineral norbergite, $Mg_3SiO_4(OH)_2$ [White, Miller & Nielsen, *Acta Cryst.* (1965). **19**, 1060–1061]. X-ray intensities were collected on a four-circle automatic single-crystal diffractometer with Zr-filtered Mo $K\alpha$ radiation. The structure has been refined from 1241 reflexions to $R=0{\cdot}031$. Both structurally independent iron atoms are surrounded by six oxygen atoms forming distorted octahedra. Boron is exclusively tetrahedrally coordinated by oxygen.

Introduction

The crystal structure of Fe_3BO_6 (White, Miller & Nielsen, 1965) has been found to be isotypic with that of the mineral norbergite, $Mg_3SiO_4(OH)_2$ (Taylor & West, 1929). In the paper of White *et al.* (1965) only mean bond distances Fe–O (2·04 Å) and B–O (1·47 Å) are reported because of the limited accuracy of the oxygen coordinates which resulted from an overlap of the oxygen positions in an *h*0*l* electron density projection. Isotropic temperature factors are given: 0·52 Å^2 for the iron atoms, 0·90 Å^2 for the lighter atoms. Fe_3BO_6 is a so-called easy-axis ferrimagnet with a Néel temperature of 235°C. In order to study the op-